N-63-4-3

410111

Examination of the perturbation of spectral frequencies by solid matrices in the vacuum ultraviolet; study of the absorption spectra of atomic species in a compressed matrix of a frozen rare gas; study of the possibility of studying the L$_\alpha$ line of atomic hydrogen in solid matrices

A B S T R A C T

The absorption bands situated at 1485 and 1295 Å unequivocally and on some spectra the weak bands at 1505 and 1370 Å for pure xenon at liquid hydrogen temperature were observed, the first two being also recorded at liquid helium temperature. These two are obviously due to the perturbed transition of Xe 1469 and 1296 Å respectively. The results are in good agreement with those of Sonnepp and Dressler (J. Chem. Phys. 33, 49, 1960) who observed 4 bands at 1508, 1485, 1360 and 1305 and with the very recent results of Baldini (Phy. Rev. 128, 1562, 1962) who used a different technique and observed 3 bands at 1485, 1360 and 1305 Å. The first line of the gas is seen to be displaced about 700 cm^{-1} towards the longer wavelength.

Per contra, in the case of xenon in a matrix of argon we observe 3 bands at 1370, 1340, 1250 Å which are obviously displaced towards shorter wavelengths relative to those of the gas. If the first band which is more intense and wider on plotting the optical density, corresponds to the resonance line of xenon 1469 Å, the displacement towards the shorter wavelength is 4950 cm^{-1} and this agrees in order of magnitude with that calculated from the extrapolation of Robin's results for gaseous Xe line in compressed argon at 20° K (989 amagats).

The values obtained for the peak absorption coefficient 5.10^{6} cm^{-1} are in reasonable agreement with those of Baldini.

All these results were the fruit of the excellent improvements in experimental technique realised which enabled us to push the limit of spectra to 1150 A and to use the liquid Helium cryostat successfully. We are much nearer to our ultimate goal of studying Lyman α line of atomic hydrogen trapped in a matrix at liquid helium temperature requiring the tackling a few more experimental problems.

- - - - - - - -

" Examination of the perturbation of spectral frequencies by solid matrices in the vacuum ultraviolet; study of the absorption spectra of atomic species in a compressed matrix of a frozen rare gas, study of the possibility of studying the Lα Line of atomic hydrogen in solid matrices "

B. VODAR : Principal Investigator

CONTRACT N° DA - 91 - 591 - E U C - 2260

FINAL TECHNICAL REPORT *

Of December 1st 1962 to March 31st 1963

* The research reported in this document has been made possible through the support and sponsorship of the U.S. Department of Army through its European Research Office

I - INTRODUCTION

The present research program is an extension of our earlier work with simple atoms like Hg and molecules like benzene in frozen matrices to the theoretically simpler use of the absorption spectra of xenon both in the pure state and in a matrix of argon. As the resonance line of Xenon 1469 A is much shorter wavelength than the Hg resonance line 1850 Å, the experimental difficulties mount up and the improvement of techniques employed in the sinc[illegible]ion of success. So a greater part of the report deals with the improvements realised so far.

As in the case of Hg, the idea of regarding the present studies with atoms in frozen matrices as an extrapolation of the observed shifts of the spectral lines due to the material, was again exploited for the case of xenon in argon.

Finally, we are much nearer to our ultimate goal of realising experimentally the extremely interesting and theoretically simple case of Lyman α line (1216 Å) of atomic hydrogen trapped in a matrix at liquid helium temperature. But we have yet to tackle a few experimental problems remaining to achieve the desired end.

II - INSTRUMENTAL PROBLEMS

Source for continuum :

Below 1650 Å, the hydrogen lamp gives a line spectrum and therefore, is no longer usable. So we tried at first to adapt the discharge in rare gases as described by Y. Tanaka (J.O.S.A. 45, 710, 1955). After some unsuccessful attempts which were traced to the impurities in the gases employed, we used the high purity Krypton and Argon furnished by Linde Co (U.S.A.) An old glass apparatus pumped by a diffusion pump served to fill the gas at pressures around the 300 mm and then the lamp was sealed off.

The electrical constants of the circuitry have not been indicated clearly by the previous authors and so we found by trial, the best intensity with a condenser of 2350 pF, a resistance of 125,000 Ω , a current of 80 m A and a voltage of 30,000 V in the secondary of a transformer, with Krypton lamp we got some positive results but the intensity was too small requiring long exposures and further it did not extend sufficiently into the ultraviolet.

So we abandoned this type of discharge lamp and utilised the three electrode vacuum spark source as described by J. Romand and G. Balloffet. It consists of a triggering spark between an anode and the body across a semi conducting material and a main spark between the uranium electrode and the body. The condenser used has a value of 0,5 μF and is directly mounted on the electrode to reduce the self inductance. The Voltage is 20.000 V and the maximum current is estimated to be 50.000 A. The sparks take place once every 2 sec. The electrode material is an uranium wire 2 mm in diameter and this gives the best intensity and continuum free from lines when properly adjusted. Its greatest inconvenience as compared to the discharge lamp is the rapid wearing out of the electrode which entails frequent adjustment of the source. Moreover, this adjustment is very critical the effective source is very small in dimensions 1 to 2 mm above the tip of the electrode. Also it was found by experience that the length of the electrode is important and the electrode should be used for some time before giving the maximum intensity. As the electrodes have to be readjusted after about 30 minutes of use, it was found convenient to isolate the spark chamber from the rest of the apparatus when desired by a valve and a separate pumping unit with a diffusion pump was installed. By this means the electrode could be adjusted or replaced, and the spark chamber pumped again within 10 minutes, further it improved the vacuum in the entire apparatus

The schematic representation of the experimental assembly is given Fig. 1

Focussing of the Source :

The source pulverises very much and hence the condensing lens of lithium fluoride used with condensed discharge lamps could not be employed. So we resorted to a reflection at an incidence angle of 60° which was a compromise between reflecting power and astigmatism both of which increase with angle of incidence.

A torroidal mirror whose radii of curvature were 20 et 80 cm produced an elonga - ted image of the quasi-point source parallel to the height of the spectrograph. This is favorable for illuminating the grating. The projected particles from the spark formed a well regulated deposit on the mirror which did not seem to diminish in a no - table fashion the reflecting power of the mirror whereas the same would have rendered a lens totally opaque in a few minutes. The source and the reflecting power of the mirror are of sufficiently constant intensity to enable intensity measurements.

Windows :

Despite the fact that the Vacuum in the chamber outside the cryostat is very good it was found absolutely essential to isolate the vacuum in the cryostat from that outside it as otherwise the deposits on the central cooled window makes it opaque to the ultraviolet. Further this is necessary to minimise losses in liquid helium when it was used. So there are three windows in the trajectory of the light path. The two outer windows were originally sealed by indium. But as this was not leak tight we adopted 0 ring seals, each window being supported between two 0 rings. The central window is at present fixed to the Copper block with the help of an indium seal and a copper screw. But some unsuccessful attempts of ejection resulted and these were finally traced to the bad thermal contact between the copper block and the window. It was necessary to screw tightly the window after every experiment. To ensure a better thermal contact by a more efficient tightening we have a new design for pressing a window of 20 mm diame - ter between two blocks by means 3 screws of 5 mm diameter. The contact will be 3 mm wide instead of the present 1 mm we have not yet used this support.

The window necessitates a thorough cleaning after each experiment and prefe - rably on the day of the experiment. With three windows of Li F and an exposure of 6 minutes we were able to push the spectrum about 1150 Å. When it was not necessary to go beyond 1250 Å, fluorite windows are to be preferred for their greater transparency and sharp cut off.

Spectrograph and Grating :

There was considerable trouble caused by parasitic illumination caused by dif - fused light and in particular that furnished by the zero order reflection which approa - ched the wall of the spectrograph and by the 1st order visible spectrum which gets re - flected in this unfavourable fashion from certain points in the spectrograph . Suitable

stops placed at appropriate places between the grating and the plate holder served to reduce considerably the parasitic illumination without suppressing it completely. Further a few stops between the slit and the exit window of the cryostat helped a little to limit the light falling on the grating so that it is just covered. But still we were bothered with stray light as the quality of the grating had deteriorated probably due to our previous experiments with mercury. So we finally replaced the Gomes grating (10.8 Å/mm) by a Bausch and Lomb grating (8.5 Å/mm) platinised and blazed for 800 Å.

With no window, when the film was over exposed for 1100 A; the spectral region near 1500 A was very feeble. With 1 window an exposure of 40 sec and with 3 windows 6 mn sufficed to bring out the spectrum up to 1150 A. Further the diffusion had completely disappeared as verified by using a bad quality Li F window or with a fluorite window which has a sharp cut off at 1250 A

Films and plate holders :

The use of a S W R Kodakfilm much faster in the ultraviolet that the sensitized plates and much less sensitive than the latter in the visible was very advantageous in eliminating any residual parasitic effects. Unfortunately as this film is only available commercially in films of 35 mm width and the manipulation is very difficult due to its extreme fragility we have adapted a modification of the plateholder in use to permit the mounting of two strips of films side by side which can be utilised successively during the same experiment and can be developed simultaneously.

One film was used for calibrating the film with neutral wire gauze filters and the other film recorded the absorption spectra of the matrix studied. There were 6 exposures on each film.

Vacuum :

Considerable improvement in the vacuum of the spectrograph was affected by connecting the diffusion pump directly below the spectrograph and replacing all the rubber tubing by metal tubing. This resulted in a vacuum of better than 10^{-4} mm in the spectrograph eliminating any traces of absorption by residual nitrogen and water vapour. The vacuum in the chamber outside the cryostat was about 5×10^{-6} mm and in the cryostat with liquid air cooling on the outside, a pressure of 1×10^{-6} mm was attained. With liquid hydrogen in the cryostat the pressure was 7×10^{-7} mm and with liquid helium 5×10^{-7} mm.

Measurement of Temperature :

We decided, after some unsuccessful attempts, to measure the temperature of the copper block holding the central window . The Cu - constantan thermocouple used is a very fine (15/100 mm) to limit the thermal losses by conduction. It is soldered to the block and it traverses the exterior wall of the cryostat through a de -

mountable glass tube to which it is permanently fixed by araldite. The mounting of the thermocouple is a delicate operation due to the presence of two interior thermal shields and the external passage.

Cryostat :

We encountered some problems with a leak developing at the O ring seal when the external liquid nitrogen envelope was filled due to the flange holding the O ring being too thin. So we soldered a water cooling tube around the neck between the two O rings seals and this seals the flanger sufficiently during the cooling of exterior envelope. It completely eliminated all our troubles with leaks at this joint.

When the interior of the cryostat is cooled initially with liquid nitrogen to save liquid hydrogen used, it takes about 10 minutes to cool the block holding the window to that temperature. Then the liquid nitrogen is blown away until the temperature of the block just rises a little to ensure complete removal of liquid nitrogen in the interior. This is essential as otherwise when liquid hydrogen is introduced it produces solid nitrogen at the bottom of the cryostat and due to its small conductivity it takes nearly more than 1 hr for the block to descend to liquid hydrogen temperature. With liquid helium, it was found desirable to first cool the cryostat with liquid hydrogen to save the consumption of liquid helium. Again, the same precaution of completely driving out liquid hydrogen before introducing liquid helium was taken.

It takes less than 5 minutes for the block to obtain that temperature. It can be maintained at about 4,2° K for nearly 1 Hr. using 2 litres of liquid helium to fill the cryostat of capacity 0.2 l.. The vacuum valve of the cryostat was closed tightly and the Balzers gauge turned off when liquid helium was used.

Collodion windows :

In order to extend further the spectrum into the ultraviolet with a view to studying Lyman α (1216 A) of hydrogen when it is displaced towards shorter wavelength we intend to replace at first the two extend windows and then central window also with collodion windows. We have already made some preliminary studies with collodion film deposited on an electron microscope copper gauze with a transparent area of 60 %. But these films were not vacuum tight. Now we are going to try a better copper gauze with a transparency of 80 % and a double layer of extremely pure collodion :
The film is floated off the surface of water on a metal frame so that it doubles up on it and then it is transferred to the metal holder.

Ejector :

Some preliminary trials indicated that the dimensions of the ejector from which one forms the jet condensing on the window of the cryostat are critical. A very narrow ejector covers only a small portion of the window and an ejector too wide causes the jet to be widely dispersed. In the case of pure Xenon we obtained a convenient condensed layer with an ejector of 0.5 to 1 mm in diameter and 2 cm in length, the pressure behind the ejector varying from 0.05 to 0.5 mm of Hg. For obtaining thin layers of Xenon in Argon; we tried at first to condense directly from a mixture of 1 part of Xenon in 300 parts of Argon prepared in advance employing the same ejector as for Xenon but with a pressure behind the ejector very much higher (5 to 15 mm of Hg). But the large difference in the masses of argon and of xenon atoms and the different partial pressures of the two gases made it impossible to control the composition of the mixture which ejected. A satisfactory solution of the problem was achieved by using separate ejectors for xenon and for argon and by calculating the necessary dimensions of the ejectors and the ratio of the pressures of the gases from the desired concentration ratio of the ejected gases. For pratical realisation a symmetric mounting a double coaxial ejector was fabricated (see figure1)

The central ejector is a stainless steel tube of 0.7 mm internal and 1.1 mm external diameter and 20 mm long; the coaxial ejector for argon is a silver tube of 0.12 mm internal diameter, length 10 mm. The useful cross section of the external diameter.length 10 mm. The useful cross section of the external diameter is equivalent o a tube of 0.5mm ϕ. If a_1, l_1, P_1 and a_2, l_2, P_2 are respectively the radii, lengths and pressures in the ejectors of argon and of xenon; one has to a first approximation

$$\frac{Q_1}{Q_2} = \left(\frac{a_1}{a_2}\right)^4 \left(\frac{P_1}{P_2}\right)^2 \left(\frac{l_2}{l_1}\right)$$

For the geometry of the ejector used, this gives :

$$\gamma = \frac{Q_1}{Q_2} \simeq 0.5 \left(\frac{P_1}{P_2}\right)^2$$

For example if $P_1 = 3$ mm, $P_2 = 0.1$ mm $\quad \gamma = 450$

One can evaluate the total amount of xenon deposited on the window from the conditions of ejection. The deposits which we have realised are of the order of $Q.\dot{1}$/sec To get useful thicknesses of deposits, the time of ejection varied between 10 sec to 80 sec.

III - RESULTS

a) Pure Xenon at 20° K

We obtained the absorption spectrum of pure xenon at 20° K first with the Krypton discharge source and then with the triggered spark source.

We observe clearly the two intense bands at 1485 and 1295 Å. On some spectra we could see the bands at 1505 and 137 0Å which are very weak. The results are in good accord with those of Schnepp and Dressler (J. Chem Phys. 33, 49, 1960) who observed the bands at 1508, 1485, 1360 and 1305 and with those of G. Baldini (Phys. Rev. 128, 1562, 1962) who observed 3 bands at 1485, 1360, and 1305 A. Thus the first line of the gas is displaced about 700 cm^{-1} towards the longer wavelengths

b) Xenon in argon at 20° K :

The curve for the optical density of the absorption spectra of xenon in argon is given in Fig 2. We observe these 3 bands with their maxima at 1370, 1340 and 1250 A. The 2nd band which is narrow appears most intense in the spectral film to the naked eye. So we took it to correspond to the 1469 A line of xenon in an earlier report. But from the microphotometer plots and calibrated intensity marks, it appears that the band at 1370 Å. is more intense and wider. So it seems now to us more reasonable to take this first band to correspond to the resonance line of xenon and the displacement is 4950 cm^{-1} towards the shorter wave length contrary to the case of pure xenon solid.

This result may be compared with that of J. Robin (Thesis, Paris 1951) for the perturbation of this line in gaseous xenon by argon from 250 to 500 amagats. In this region Robin noted that the displacement of this line varies more quickly than the square of the density of argon and can be represented by the formula :

$$\Delta \nu = a \rho^2 + b \rho^3$$

where a = 1.1 x 10^{-3} cm^{-1} per amagats ^{2} and b = 5.8 x 10^{-6} cm^{-1} per amagat ^{3}. When this is extrapolated to the density of solid argon at 20° K (990 amagats) it yields $\Delta \nu$ = 6700 cm^{-1} which is in fair enough agreement with our experimental results in the order of magnitude, as any closer agreement is illusory.

c) Xenon pure and in argon at liquid helium temperature :

The curve for the optical density of the absorption spectra of pure xenon at 4 4° K is given in Fig. 2. The two bands reported by Dressler at 1508 and 1370 A were not observed by us at this temperature while they are visible on some spectra at 20° K.

But this cannot be definitely attributed to a temperature effect as the displacements are the same at the two temperatures.

d) Absorption coefficients :

Using the formula for gas flow (Dushman's vacuum technique p. 841)we get for the ejector used

$M_g \sim 6 \times 10^{-6} P^2$ g of xenon/sec where P is in mm of Hg

This gives for the pressures used and the size of the window, the rate of flow of xenon

$\sim$ 0.1 Å/sec.

This is also the rate of the equivalent xenon thickness in the case of xenon in argon.

The calculated absorption coefficient for the film thickness used turns out to be about 10×10^6 cm^{-1} (for 1485 Å band) in the case of pure xenon and 5×10^6 cm^{-1} (for 1340 Å band) in the case of Xenon in argon. This compares reasonably with Baldini's value of 3×10^6 cm^{-1}

I V - FUTURE PROGRAM

A - Apparatus :

As remarked earlier we are trying to make windows of collodion to replace the two external windows of the cryostat.

We expect to regulate the height of the electrode by means of an automatic (clockwork) mechanism and thus have greater stability in the intensity of the source.

We are awaiting the delivery of the Bausch and Lomb grating with an improved aluminium coating and a magnesium fluoride protective layer, expected to give an increase of intensity in the range 1200 - 1500 Å

B - Studies :

The following studies are envisaged in the future :

1) Continuation of the study of xenon in a matrix of krypton which will permit a comparaison of the displacements of the bands of longer wavelength while those of shorter wavelength will be masked by the absorption of solid Krypton at 1236 Å

2) The absorption of pure krypton and in a matrix of argon.

3) The Lyman α (1216 Å) of atomic hydrogen at liquid helium temperature if we have success with collodion windows.

4) Higher terms of the principal series of the alkali elements in a matrix.

Personnel involved during the Research period :

- Boris VODAR	Principal Investigator	
- Jacques ROMAND	Dr. ès Sc. Res. Scientist	(part time)
- Mme M. DAMANY - ASTOIN	Dr. ès Sc. Res. Scientist	(part time)
- V. CHANDRASEKHARAN	Dr. Sc. Visiting Scientist	(full time)
- Jean Yves RONCIN	Licencié ès Sc. Res. Assistant	(full time)

- - - - - - - - -

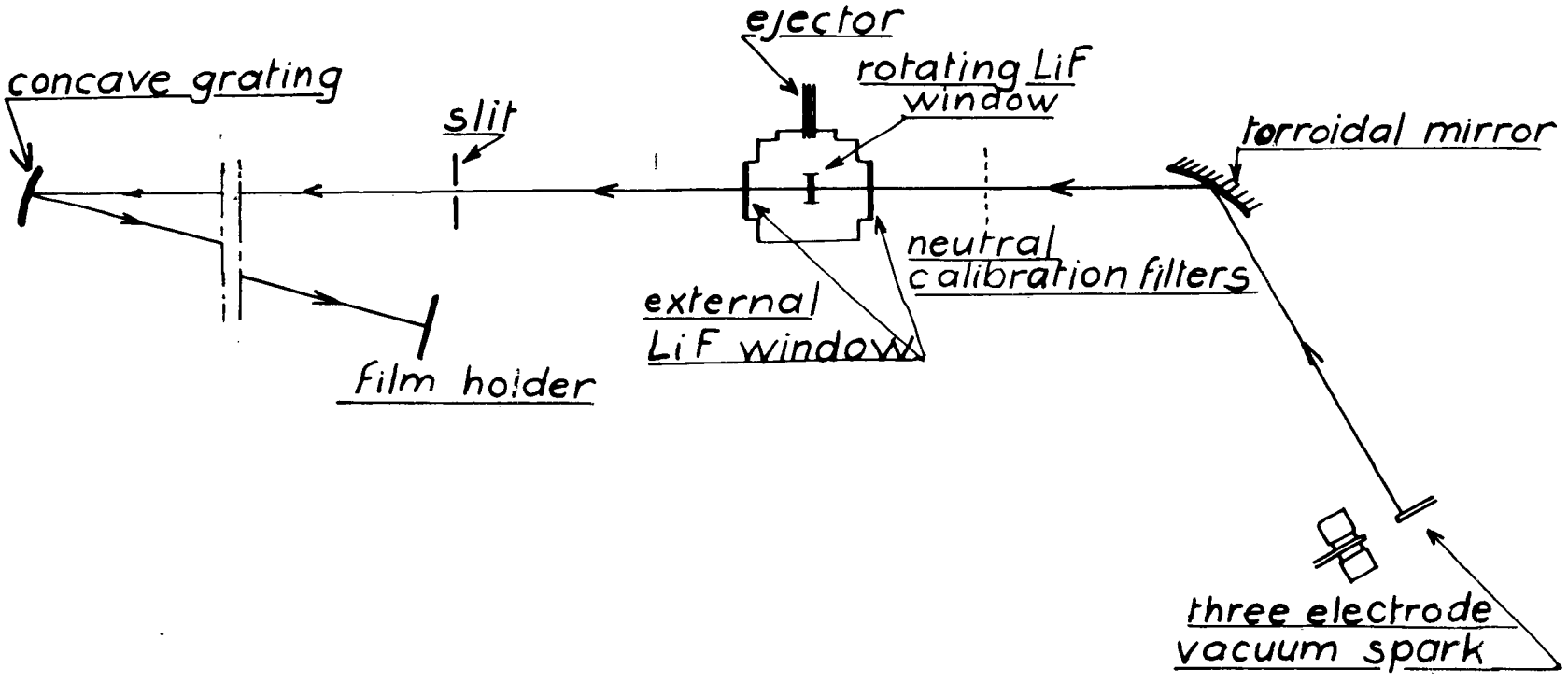
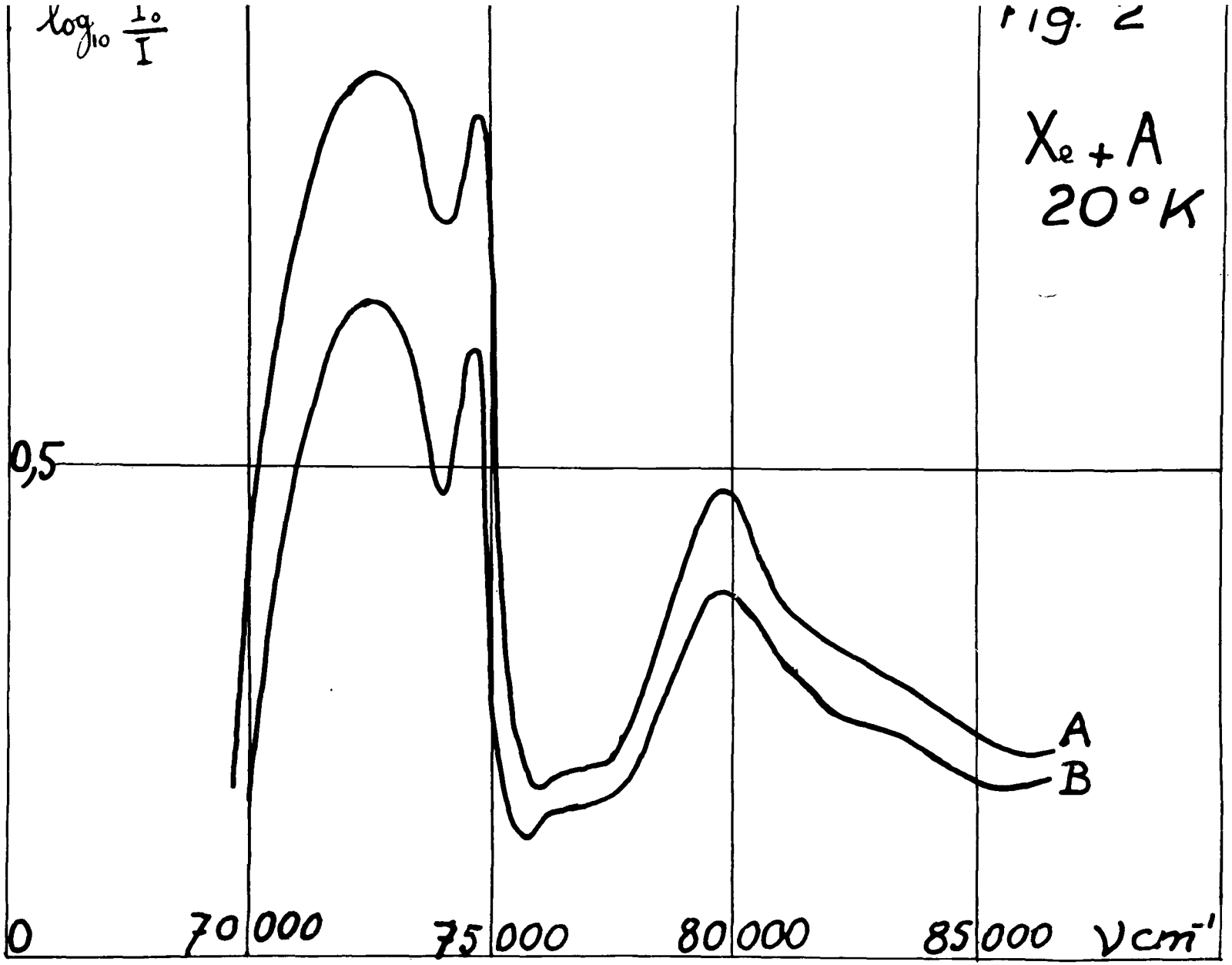

concave grating
slit
ejector
rotating LiF window
toroidal mirror
neutral calibration filters
external LiF window
film holder
three electrode vacuum spark

Fig. 1


log10 I0/I
fig. 2
Xe + A
20°K
0,5
A
B
0
70 000
75 000
80 000
85 000
ν cm⁻¹

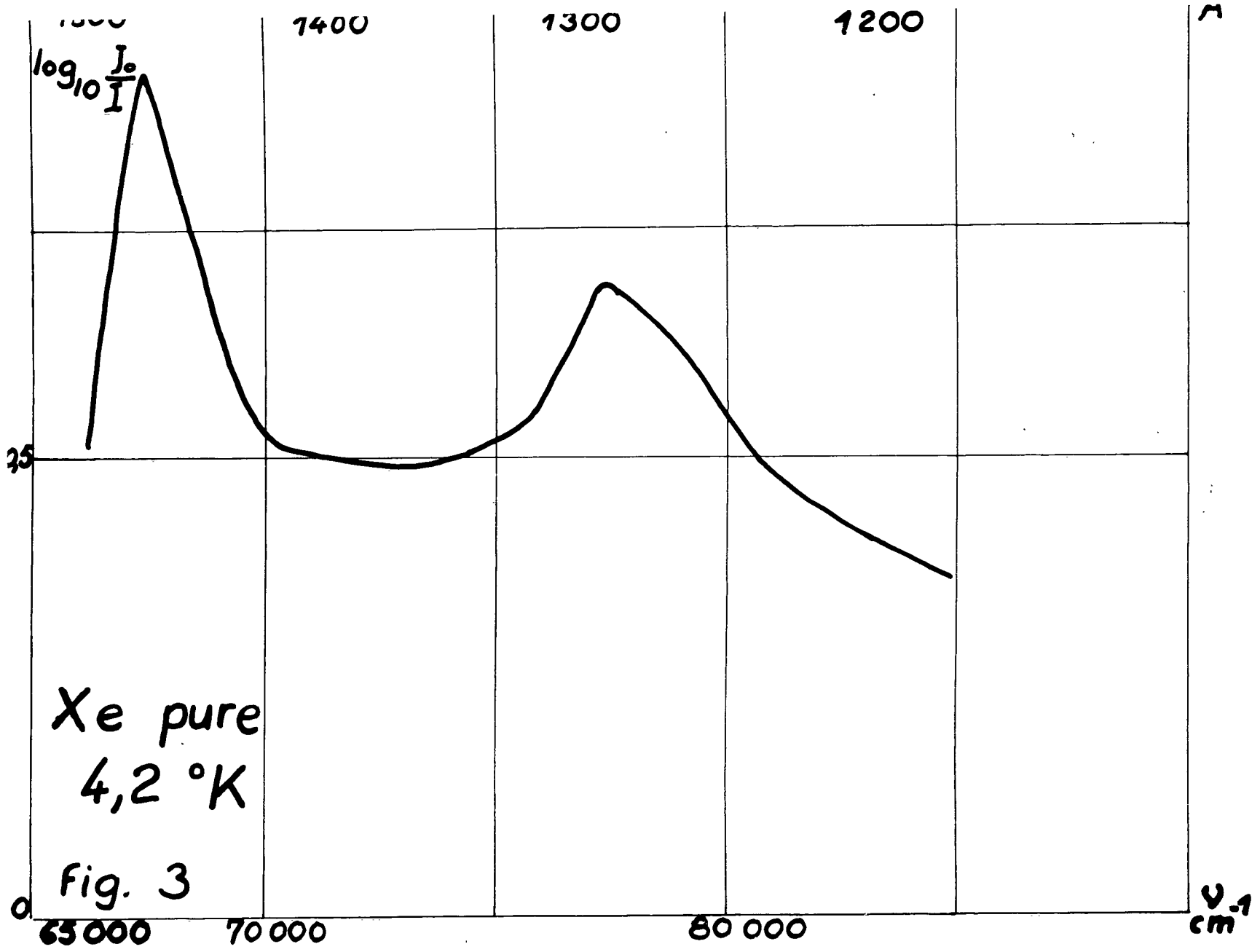

1400
1300
1200
$\log_{10} \frac{I_0}{I}$
0,5
0
Xe pure
4,2 °K
65 000
70 000
80 000
ν cm^{-1}

Fig. 3